

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 October 2003 (23.10.2003)

PCT

(10) International Publication Number
WO 03/087015 A1

(51) International Patent Classification⁷: C04B 35/58, C22C 29/18, H05B 3/14

(21) International Application Number: PCT/SE03/00380

(22) International Filing Date: 6 March 2003 (06.03.2003)

(25) Filing Language: Swedish

(26) Publication Language: English

(30) Priority Data:
0201043-7 5 April 2002 (05.04.2002) SE

(71) Applicant (for all designated States except US): SANDVIK AB [SE/SE]; S-811 81 Sandviken (SE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SUNDBERG, Mats [SE/SE]; Liljanstorpssvägen 57, S-722 46 Västerås (SE).
PETTERSSON, Hans [SE/SE]; Rallsta 20B, S-734 91 Hallstahammar (SE).

(74) Agents: ÖRTENBLAD, Bertil et al.; Noréns Patentbyrå AB, Box 10198, S-100 55 Stockholm (SE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF MAKING A HEATING ELEMENT OF MOLYBDENUM SILICIDE TYPE AND A HEATING ELEMENT

(57) Abstract: The present invention relates to a method for the production of a heating element that is comprised essentially of molybdenum silicide and alloys of this basic material. The invention is characterised by producing a material that contains substantially Mo (Si_{1-x}Al_x)₂ and Al₂O₃ by mixing a molybdenum aluminium silicide Mo (Si_{1-y}Al_y)₂ with bentonite clay in a manner known per se, wherein the bentonite clay is caused to contain impure or contaminating substances with which molybdenum silicide cannot be alloyed and with which the symmetry of the crystal lattice of the molybdenum silicide is retained with a combined content of less than 2000 ppm. The invention also relates to a heating element.

WO 03/087015 A1



Method of making a heating element of molybdenum silicide type and a heating element.

The present invention relates to a method of manufacturing a heating element of the molybdenum silicide type and also to a heating element.

An electric resistance element of the molybdenum silicide type is described in Swedish Patent Specifications 0003512-1 and 0004329-9. According to patent specification 0003512-1 the resistance material of the heating element includes $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ which is caused to contain aluminium to an extent at which the formation of pest is essentially prevented.

It has been found that when such material is operated in a temperature range of 400 - 600°C no pest, or only a slight amount of pest, is formed. Pest is formed by virtue of the formation of MoO_3 from MoSi_2 and O_2 .

The reason why the formation of pest is significantly reduced or is eliminated is due the formation of Al_2O_3 on the surface of the element.

According to one preferred embodiment x is caused to lie in the range of 0.2 - 0.6.

The other patent specification 0004329-9 teaches a method of increasing the useful life span of heating elements that consist chiefly of molybdenum silicide and alloys of this basic material where the element operates at high temperatures.

According to this patent specification, the heating element is caused to contain aluminium to an extent which is suffi-

cient to maintain a stable, slowly growing layer of aluminium oxide on the surface of the heating element.

According to a preferred embodiment the heating element material is caused to contain $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ where x lies in the range of 0.2 - 0.6.

A material of the molybdenum silicide type that contains aluminium has been found to possess improved corrosion properties at both low and high temperatures.

Such material is often produced by mixing MoSi_2 powder with oxidic raw material, such as aluminosilicates. When the raw material is bentonite clay, there is obtained a relatively low melting point which contributes towards so-called smelt phase sintering which results in dense materials that contain MoSi_2 and a proportion of aluminium silicate corresponding to 15 - 20 percent by volume.

Bentonite clay has different compositions. Some bentonites include 60% by weight SiO_2 while some contain somewhat more than 70% by weight SiO_2 . Although the Al_2O_3 content varies, it normally lies between 13 - 20% by weight. The melting point varies between about 1200 - 1400°C.

25

Bentonite clay that contains chiefly SiO_2 can be used in the production of heating elements containing $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$. When sintering with an Al-alloyed silicide there takes place a chemical exchange reaction in which the greater affinity of the oxygen to Al than to Si results in Si leaving the aluminium silicate and entering the silicide as a result of Al leaving the silicide and being sucked up by the oxide phase. This exchange reaction also contributes towards improved sin-

tering properties of the composite material. The final material contains $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ that is substantially deplete of Al, where the oxide phase contains Al_2O_3 in all essentials.

5 The standard procedure of manufacture involves mixing molybdenum, silicon and aluminium in powder form and firing the powder mix normally under a shielding gas atmosphere. This results in a cake of the material $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$, where y is larger than x as a result of said exchange reaction. The re-
10 action is exothermic. The cake is then crushed and ground down to a fine particle size normally in the order of 1 - 20 μm . This powder is mixed with bentonite clay such as to form a wet ceramic material. The material is extruded and dried to a rod form whose diameter corresponds to the diame-
15 ter of the subsequent heating element. The material is then sintered at a temperature that exceeds the melting temperature of the including components.

However, there is a drawback with an element of this kind.
20 The problem is that the oxide that forms on the surface of the element, namely Al_2O_3 , sometimes peels away or flakes off, i.e. loosens from the surface of the element in cyclic operation.

25 A peeling oxide gives poorer protection against continued oxidation of aluminium which becomes impoverished in the outer surface of the element more quickly. Moreover, peeling oxide can contaminate the oven in which the element is fitted, with the risk that performance and the appearance of products heat
30 treated in ovens that have such elements will be significantly impaired. This restricts the use of such elements in heating processes.

This problem is solved by the present invention.

The present invention thus relates to a method of producing a heating element that is comprised substantially of the molybdenum silicide type and alloys of this basic material and is
5 characterised by producing a material that contains chiefly $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ and Al_2O_3 by mixing molybdenum aluminosilicide $(\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2)$ with bentonite clay in a way known per se, where the bentonite clay is caused to include impurities with
10 which the molybdenum silicide cannot be alloyed and with which the symmetry of the crystal lattice of the molybdenum silicide will be retained, with a combined content of 2000 ppm.

15 The present invention also relates to a heating element of the kind having the significant features set forth in the accompanying Claim 7.

The invention will be described in more detail in the following.
20

In accordance with the invention, a heating element that consists chiefly of molybdenum silicide type and alloys of this basic material is produced in principle by the method described above. There is thus produced a powder that contains
25 essentially $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$ which is mixed with bentonite clay that contains Al_2O_3 .

According to the invention, the bentonite clay is caused to
30 include impurities with which the molybdenum silicide cannot be alloyed, so that the symmetry of the crystal lattice will be retained, with a combined content of less than 2000 ppm. Bentonite clay that has these low impurity contents can be

produced by purifying the bentonite clay with the aid of known chemical cleaning processes.

In distinction to this approach, it is possible to partly substitute molybdenum with Re or W in the material
5 $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ without changing the symmetry of the crystal lattice.

According to one preferred embodiment of the invention, the
10 combined content of the impurity substances Mg, Ca, Fe, Na and K is caused to be below 2000 ppm.

According to another preferred embodiment of the invention, the content of said impure substances is caused to be below
15 1000 ppm.

It has been found surprisingly that there is obtained at such low contaminant contents an oxide which does not peel after cyclic operation between room temperature and high temperature,
20 for instance 1500°C.

According to one embodiment x is caused to lie in the range of 0.4 - 0.6.

25 According to one preferred embodiment x is caused to lie in the range of 0.45 - 0.55.

The present invention thus solves the problem mentioned in the introduction and enables the present element to be used
30 beneficially in ovens without detriment to the material treated in the oven.

The present invention shall not be considered to be limited

to the aforescribed embodiments since variations can be made within the scope of the accompanying claims.

5

10

15

20

25

30

CLAIMS

1. A method of producing a heating element that is comprised essentially of molybdenum silicide type and alloys of this
5 basic material, characterised by producing a material that contains substantially $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ and Al_2O_3 by mixing a molybdenum aluminium silicide $\text{Mo}(\text{Si}_{1-y}\text{Al}_y)_2$ with bentonite clay in a manner known per se, wherein the bentonite clay is caused to contain impure substances with which molyb-
10 denum silicide cannot be alloyed and with which the symmetry of the crystal lattice of the molybdenum silicide is retained with a combined content of less than 2000 ppm.
2. A method according to Claim 1, characterised
15 in that the combined content of the impurities Mg, Ca, Fe, Na and K is caused to be less than 2000ppm.
3. A method according to Claim 1 or 2, character-
ised in that the content of said impurities is caused to
20 be less than 1000ppm.
4. A method according to Claim 1,2 or 3, character-
ised in that x is caused to lie in the range of 0.4 - 0.6.
- 25 5. A method according to Claim 1, 2 or 3, character-
ised in that x is caused to lie in the range of 0.45
- 0.55.
6. A method according to Claim 1, 2, 3 or 4, character-
30 ised by substituting molybdenum partly with Re or W in the material $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$.

7. A electrical heating element that is comprised substantially of the molybdenum silicide type and alloys of this basic material, characterized in that said element is comprised chiefly of the materials $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ and Al_2O_3 ,
5 in that the material contains impure substances with which the molybdenum silicide can not be alloyed and with which the symmetry of the crystal lattice of the molybdenum silicide is maintained with a combined content of less than 2000ppm.
- 10 8. A heating element according to Claim 7, characterized in that the combined content of the impurities Mg, Ca, Fe, Na and K is caused to be less than 2000ppm.
- 15 9. A heating element according to Claim 7 or 8, characterized in that the impurity content of said material is less than 1000ppm.
- 20 10. A heating element according to Claim 7, 8 or 9, characterized in that x lies in the range of 0.4 - 0.6.
11. A heating element according to Claim 7, 8 or 9, characterized in that x is caused to lie in the range of 0.45 - 0.55.
- 25 12. A heating element according to Claim 7, 8, 9, 10 or 11, characterized in that molybdenum in the material $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ is replaced partially with Re or W.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00380

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 35/58, C22C 29/18, H05B 3/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B, C22C, H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 731616 A (METRO-CUTANIT LIMITED), 8 June 1955 (08.06.55) --	1-12
A	WO 9531417 A1 (MICROPYRETICS HEATERS INTERNATIONAL), 23 November 1995 (23.11.95), abstract --	1-12
A	US 5965051 A (NORITOMO HIRAYAMA ET AL), 12 October 1999 (12.10.99), abstract --	1-12
A	GB 751294 A (METRO-CUTANIT LIMITED), 27 June 1956 (27.06.56) -- -----	1-12

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 June 2003

Date of mailing of the international search report

18-06-2003

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Ulrika Nilsson/MP
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/06/03

International application No.
PCT/SE 03/00380

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
GB	731616	A	08/06/55	NONE	
WO	9531417	A1	23/11/95	AU 2464595 A AU 2606895 A US 5611953 A WO 9531416 A	05/12/95 05/12/95 18/03/97 23/11/95
US	5965051	A	12/10/99	DE 19602141 A JP 3230793 B JP 8198680 A	01/08/96 19/11/01 06/08/96
GB	751294	A	27/06/56	NONE	